



# **COMPOUNDING OF PHOSPHAZENES FOR MILITARY APPLICATIONS**

**BY**

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## Preface

The work reported here was conducted over a number of years as part of an attempt to obtain the ideal military elastomer. This ideal elastomer would be flexible in the arctic, stable in the tropics and nonflammable. Essentially this means the material must possess a glass transition temperature of  $-50^{\circ}\text{C}$ , lack of tackiness at elevated temperatures and nonflammability in all possible military environments. The polyphosphazene polymers possess these properties and are also quite resistant to petroleum products. Difficulties in the high price may limit broader application of this material to military items at this time, but it is imperative that we follow developments in this material. This was the reason for the Polyphosphazene Conference 6-7 November 1985 at The United States Naval Academy at Annapolis, Maryland, sponsored by the Navy and for the presentation at that conference upon which this paper is partially based.

The commercial terms used for the various compounding ingredients are not always known to the reader. For this reason a description of them is given in the appendix.



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COMPOUNDING OF PHOSPHAZENES FOR  
MILITARY APPLICATIONS

INTRODUCTION

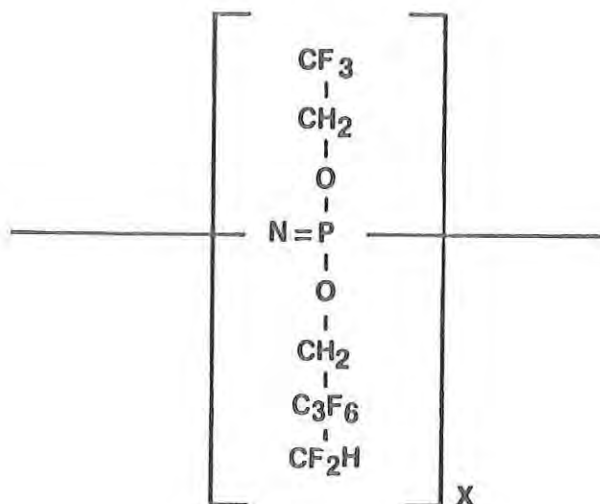
The objective of this report is to review the polyphosphazene compounding work conducted at the US Army Natick R&D Center. The compounding work is of interest because in the future polyphosphazenes will be supplied in a compounded form by companies like Ethyl Corporation in the U.S. or Shin Nisso Kaka Co. in Japan rather than as the pure gum previously available.

The uses that were made of the compounded polyphosphazene will also be highlighted, as it has been observed that every time a polyphosphazene material is actually introduced into an end item, either military or civilian, the impetus for additional research work increases. The additional research work in turn can lead to a better and/or less expensive product. In this same vein the work will also be discussed where we made a product but did not subsequently introduce such a product into the system. This portion of the work is reported to highlight opportunities for greater use of polyphosphazenes and to define any shortcomings in the material that industry, government, or academia may be able to correct.

Some of the work discussed will be eighteen years old. The older work is presented partly to show how much practical information can be obtained from only an ounce or so of a new elastomer. The author would like to acknowledge that this work was conducted during the late 60s and 70s as well as in the 80s mainly by the co-author, Mr. Angus Wilson, and by Mr. Patrick Mahoney in the Polymer Branch of the present Individual Protection Directorate (IPD) at Natick under the leadership of Dr. Malcolm Henry, who served for a portion of that time in two capacities in the Individual Protection Laboratory -- Chief of the Polymer Branch and Assistant Laboratory Director. It was Dr. Henry's vision that was responsible for the enthusiasm shown for the new polymer.

## DISCUSSION

Copolymer. The work on compounding polyphosphazenes started at the U. S. Army Natick R&D Center in the period 1967 to 1968. About one ounce of polyphosphazene gum of the so-called copolymer type described in the composition below was obtained from Dr. Selwyn H. Rose of the Horizons Corporation.<sup>1</sup> The polyphosphazene was of the fluoro-alkyl type discussed in some detail in numerous articles.<sup>2,3,4</sup> The chemical structure is shown in Fig. 1.



### LEGEND

SOFT, TRANSLUCENT, AMBER GUM

DENSITY: 1.6 g/cm<sup>3</sup>

SOLUBLE: ACETONE, MEK, ALCOHOL

INSOLUBLE: BENZENE, 70/30 ISOOCTANE/TOLUENE

Figure 1. The copolymer polyphosphazene gum.

Numerous compounding studies were conducted using two different curing agents, different compounding ingredients, bin aging, and different curing cycles. Some of these compounds recipes are defined in Table A-1 in the Appendix.<sup>5</sup> Regardless of the heroic measures used, it appeared to be impossible to achieve a tensile strength above 1000 psi. Other properties, such as low-temperature flexibility, oil resistance, and flame resistance, were examined from the small amounts of polymer compounded. For this combination of properties, polyphosphazene was superior to all other elastomers. Table A-2 in the Appendix lists the important properties of mostly generic elastomers, and the superiority of polyphosphazene is quite dramatic. Taking just one property, low temperature flexibility, only silicones, natural rubber, and butyl rubber can compete, and these polymers have other deficiencies such as lack of oil resistance and/or flammability.

Terpolymer. Test results on the copolymer generated enthusiasm and financial support. The support in turn resulted in the so-called terpolymer in which the introduction of an allylic moiety allowed for cross-linking. Table 1 shows some of the markedly improved mechanical properties that resulted, using either a silica-based or carbon-black based reinforcement filler.

TABLE 1. Terpolymer - Filler Evaluation

	<u>Silica-Based</u>	<u>Carbon-Black-Based</u>
	<u>(in parts per hundred)</u>	
Polymer	100	100
XLC Magnesium	6	6
SilanoX 101*	35	- -
Sterling S0**	- -	30
Dicup 40C	1	2
Tensile, KPA (psi)	13,435 (1950)	11,020 (1600)
Elongation, %	200	165
Shore A	46	50

\* Hydrated Silica

\*\* Carbon Black

Note that these two compounds were prepared with a peroxide cure. Dicumyl 40C is a dicumyl peroxide compound. Compounds were also prepared using a sulfur cure as shown in Table 2.<sup>6</sup>

TABLE 2. Sulfur-Cured Phosphazene Rubber Polymer K17621  
by Batch Number (in grams)

Compound	105-1A	105-1B	107-1A	107-1B
Polymer K17621	100	100	100	100
Silanox 101	30	30	-	-
HAF Black	-	-	30	30
Zinc Oxide	5	5	5	5
Stearic Acid	2	1	2	1
Sulfur	0.3	0.8	0.3	0.8
Sulfasan R	1	-	1	-
Butyl Zimate	2	-	2	-
Methyl Zimate	2	-	2	-
Tetrone A	-	0.3	-	0.3
Captax	-	0.5	-	0.5
Methyl Tuads	-	0.3	-	0.3
80% Tellurac	-	0.3	-	0.3
Press Cure, Min/°C	60/149°	60/149°	60/149°	60/149°
Oven Cure, Min/°C	60/149°	60/149°	60/149°	60/149°
Physical Properties:				
Modulus at 100%, MPa <sup>a</sup>	1.38	1.03	1.55	2.24
Tensile Strength, MPa	10.9	11.6	6.48	6.69
ULT. Elongation, %	300	475	350	290
Tension Set, % <sup>b</sup>	44	65	50	33
Shore A Hardness	59	57	60	64
Density, g./cc	1.72	1.72	1.69	1.72
Volume Swell, % <sup>c</sup>	25.6	26.3	19.9	17.2
Low-temp. Stiffness <sup>d</sup>				
T <sub>2</sub> , °C	-11°	-11°	-5°	-11°
T <sub>5</sub> , °C	-40°	-36°	-27°	-39°
T <sub>10</sub> , °C	-51°	-48°	-42°	-51°
T <sub>100</sub> , °C	-67°	-67°	-63°	-68°

<sup>a</sup>MPa - Mega Pascal Pressure, stress lb/in<sup>2</sup> x 0.006895 = megapascals (MPa)

<sup>b</sup>Percent recovery 5 minutes after pulling tensile dumbbell

<sup>c</sup>48 hours immersion in solvent of 70% Isooctane, 30% Toluene

<sup>d</sup>Gehman D-1053-79

Again we have used Silanox 101 and carbon black as reinforcing agents. The hydrated silica in general appears to give higher strength compounds than the carbon black. This was also true for the peroxide cured system. The moduli at 100% elongation are given in SI units, but if the values are multiplied by 145, values in psi result. These values then range from 150 to 325 psi, which are low enough to ensure the flexibility desired of elastomeric products such as gloves. Volume swell studies were conducted with the mixed solvent toluene-isooctane and are generally lower for the carbon black reinforced compounds. All four values shown compare favorably with values that would be obtained with competing elastomers.

Lohr at Firestone has made a comparison of equilibrium volume swell of the polyphosphazene terpolymer with competing elastomers.<sup>6</sup> However, he used toluene alone. At 23°C he obtained a swelling value of less than 15% for the terpolymer compared to 19% for fluorosilicone, 25% for fluorocarbon, 142% for silicone, 150% for polyepichlorohydrin, and 430% for polyacrylate polymers. This resistance to toluene was also corroborated by more practical swelling studies in ASTM Fuel C, Aviation 100, JP-4, Arctic diesel, and ASTM Fuel D/Ethanol. The swelling was 20% or less in every case. Lohr did point out the deficiency of the polyphosphazenes in some hydraulic fluids that were based upon alkyl phosphates. Skydol for example swells the polyphosphazenes over 150%. In any event, the excellent fuel resistance, now combined with greatly increased strength due to the added crosslinking monomer, encouraged the preparation of venturesome articles impossible to prepare with the original weak copolymer.<sup>7</sup>

#### GLOVE PREPARATION

It was well known that those end items to be molded or calendered could easily be prepared from polyphosphazene elastomers. On the other hand, thin-walled complex shaped items, such as gloves, are best made by dipping either porcelain or metal forms into compounded rubber latex or solvent cement, then drying and curing the finished item thus formed. It was decided to utilize polyphosphazene for such a product because of its low temperature flexibility, its resistance to petroleum solvents and its flame resistance - all properties needed in military gloves. Polyphosphazene gums designated as K17217 and K17638 terpolymers were obtained from Firestone and compounded with fillers such as Silanox 101 or Sterling SO FEF carbon black (30 to 35 parts per hundred of rubber by weight), 6 parts of XLC magnesia and 3 parts of Dicap 40C (40% dicumyl peroxide). Next, cements were prepared in methyl alcohol, methyl ethyl ketone, or a mix of the two solvents by adding small cut-up pieces of the compounded rubber to the solvent in a cement churn or ball mill. Dipping test tubes into the cements (multiple dipping and drying) produced films that could be tested for optimum physical properties. The optimum solvent found was methyl ethyl ketone. The Silanox 101 reinforcement gave a relatively stronger film, but the FEF black reinforcement gave much better tear strength.

TABLE 3. Properties of Polyphosphazene Films

<u>Reinforcement</u>	<u>Tensile Strength</u>	<u>Tear Strength</u>
Silanox 101 Reinforced	978 psi (6740 kpa)	Poor
FEF black	820 psi (5654 kpa)	Good
Silanox 101 Reinforced*	490 psi (3390 kpa)	Poor
FEF black*	209 psi (1441 kpa)	Good

\* These samples were prepared without the Hydrostone coating

The tear strengths were only determined qualitatively by the difficulty in removal from the test tube without tearing. A very important point is that a plaster coating was used to cover the polyphosphazene before autoclaving at 160°C for 30 to 45 minutes. The very low tensile results obtained when the plaster coating was not used are also shown in Table 3.

Based upon those film results, a glove was prepared by multiple dipping of a porcelain form into the cement utilizing the FEF black reinforced polyphosphazene in methyl ethyl ketone. This was of course just a feasibility study, and the cements need further optimization even to the extent of changing the curing system to allow a simpler autoclaving cure without the use of Hydrostone (plaster). The possibility also exists for using the phosphazene cement as just a coating for say a butyl glove. A picture of the monolithic polyphosphazene glove is shown in Fig. 2. A cement was prepared of the polymer in methylethylketone and a form was dipped into the cement many times to produce a glove. The glove stayed at this preprototype stage because of problems of durability and expense. However, the impetus for such a development still exists, namely the need for a glove for dispensing fuel in the Arctic at  $-50^{\circ}\text{C}$ .



Figure 2. Illustration of the glove prepared from polyphosphazene cement.

The subject of low temperature flexibility should perhaps be discussed in more detail at this point because of its importance to military items. Many commercial polymers in their brochures list the brittleness temperature; the temperature where an impact test will cause fracture (ASTM D-746).<sup>8</sup> This temperature is of course important but is only one of our requirements. It is usually necessary that an elastomer not only be free from brittleness but also that it be flexible at the very low temperatures experienced in the arctic. Again the commercial brochures may list a  $T_g$  (glass transition temperature) which is determined by thermal analysis. The temperatures acquired in this manner are generally lower than by a mechanical test. The mechanical test used most often at US Army Natick RD&E Center is the so-called "Gehman test" (ASTM-1053).<sup>9</sup> This involves a twist recovery which is more indicative of flexibility at low temperatures. The values obtained for the polyphosphazene elastomer are given in Table 4.

TABLE 4. Low Temperature Properties of Polyphosphazene

Gehman Torsional Stiffness (D-1053)	
<u>Relative Stiffness</u>	<u>Temperature (°C)</u>
$T_2$	-47°C
$T_5$	-54°C
$T_{10}$	-57°C
$T_{100}$	-66°C

If we take the temperature for  $T_5$ , -54°C (-66°F) the meaning is that the torsional stiffness has increased by a factor of five times when the temperature is reduced from room temperature to -54°C. The values obtained for other elastomers tested at NRDEC are given in Table 5. Note that in this case only the  $G_{10}$  or  $T_{10}$  is given. Viton is a fluoroelastomer with good solvent resistance. Hydrin is a polymer of epichlorohydrin. The numbers which follow the word Hydrin show whether a copolymer or a homopolymer was used. Note that NBR, the copolymer of acrylonitrile and butadiene, has greater solvent resistance and higher glass transition temperature as the amount of acrylonitrile is increased.

TABLE 5. Low Temperature Flexibility  
of Polymers by Gehman Twist Test

	<u>G<sub>10</sub> Temperature*</u>
Fluorosilicone	-60°C
Phosphazene	-57°C
Butyl	-48°C
Hydrin 200	-41°C
Neoprene	-36°C
NBR (33% ACN, 20 parts plasticizer)	-35°C
7-mil Neoprene/19-mil Butyl	-35°C
PVC (Plastisol)	-25°C to -32°C
NBR (22% ACN)	-29°C
Hydrin 100	-22°C
Low Pigment Viton	-13°C
High Pigment Viton	-10°C
NBR (41% ACN)	- 7°C
CPE	- 3°C

\* G<sub>10</sub> is the temperature where the modulus has increased  
by a factor of 10.

Glass transition temperatures are also measured by thermal analysis. This technique gives lower values, and the figures for polyphosphazene and other elastomers would be lower.

Singler has listed glass transition temperatures for polyphosphazenes determined by thermal analysis. The polyfluorophosphazene polymer has a glass transition temperature of -68°C by this method.<sup>10</sup> It is also important to note that if we want flexibility at low temperatures, the material must be flexible already at room temperature.

For example the company brochure on a material such as EVA (ethylene vinyl acetate) lists use temperatures as low as  $-40^{\circ}\text{C}$ , depending upon the copolymer composition. If one looks at the stiffness in bending, it is found that at  $-29^{\circ}\text{C}$  it is five times that at room temperature (800 psi) for the copolymer with the highest percentage of vinyl acetate (33%). The EVA with the lowest percentage of vinyl acetate (9.5%) only increases its stiffness 3.5 times at  $-20^{\circ}\text{C}$ , but it already has a bending stiffness of 14,000 psi at room temperature.

This brings up ASTM method D 797 "Young's Modulus at Normal and Subnormal Temperatures".<sup>11</sup> In this test a rectangular cross section is subjected to flexure at different temperatures and the modulus in flexure determined. When a limiting modulus is obtained (10,000 psi), that temperature is recorded. A method such as this could be used to compare the absolute stiffness of different elastomers at low temperatures. Some of the common methods of low temperature testing are given in Table A-5.

#### COATED FABRICS

The subject of coated fabrics is closely associated with that of dipped gloves, as it also utilizes a cement. Again, the same terpolymer with 1% of a cross-linking moiety (K 17638 from Firestone) was used, and both white and black cements prepared. The recipes used are given in Table 6 with all quantities expressed as pph (parts per hundred) based upon the quantity of elastomer used.<sup>12</sup>

TABLE 6. Compounding Ingredients for Coating Cement  
(in parts per hundred)

<u>Ingredients</u>	<u>CW-16 (Black)</u>	<u>CW-17 (White)</u>	<u>CW-18 (White)</u>
Polyphosphazene Rubber (K17638)	100	100	100
XLC Magnesia	6	---	---
FEF Block	30	---	---
Hydral 710	---	100	100
Aerosil 200	---	2.5	2.5
Dicup 40 C 3	3	1.75	---
2,4 Dichloro Benzoyl Peroxide	---	---	---

Cements were prepared in methyl ethyl ketone and initially applied to a light rayon fabric (3.77 oz/yd<sup>2</sup>). Because there was some apprehension concerning the adhesion of the coating to the fabric, the use of anchor coats such as Chemlock 607 and Chemlock 246 was considered. Using CW-17 for the coating, the Clark stiffness was 6.9 cm for the resulting coated fabric without the anchor coat and 13.7 cm for coated fabric utilizing either anchor coat. The higher value is indicative of greater stiffness and would probably be unacceptable in an end item. The coatings were then applied to the 4-oz/yd<sup>2</sup> polyester fabric used in the MUST (Medical Unit Self Transportable) shelter. The coatings applied encompassed but did not exactly match the coated fabric weight of the MUST fabric. The comparison of tear strengths and breaking strengths is also furnished in Table 7.

TABLE 7. Properties of Polyphosphazene Coated Fabrics  
Compared to the MUST Shelter Fabric

	<u>CW-16 (Black)</u>	<u>CW-17 (White)</u>	<u>MUST</u>
Weight, g/m <sup>2</sup>			
Base Fabric	136	136	136
Coated Fabric	427	529	502
Add On	291	393	366
Ratio	2.1	2.9	2.7
Breaking Strength, N			
Warp	801	890	1097
Fill	632	663	921
Tear Strength, N			
Warp	105	79	44
Fill	57	51	35

Breaking strength is a little low for the polyphosphazene coated fabrics but the tear strength (a more important property) is higher for the polyphosphazene coated fabrics. Besides the MUST shelter, such coated fabrics could also be used for rocket fuel handlers suit, where the natural flame resistance would be advantageous.

Very recently the Ethyl Chemical Group has been exploring methods of improving the adhesion of polyphosphazene cements to fabrics and to other elastomers. Tie coats such as Union Carbide's A 174 silane and Lord's Chemlock 607 have proved useful, as has the use of mixed solvents in which special care is taken to keep the alcohol portion completely anhydrous. Ethyl is also concentrating on the use of 2,4 Dichloro benzoyl peroxide as the cure. Only one of the samples in Table 4 used that curing agent, and perhaps that was not fully exploited.

The flammability results obtained on some representative fabrics are shown in Table 8. Note that the white coated fabric utilizing the same fabric as used in the MUST shelter had a higher Limiting Oxygen Index (LOI), showed essentially equivalent performance utilizing method 5903,<sup>13</sup> and exhibited shorter after flame and a lower percent consumed when exposed to the more severe ASTM method 5905.<sup>14</sup>

TABLE 8. Flammability Results on Coated Fabrics

	<u>Light Weight Rayon Fabric</u>		<u>MUST Shelter Fabric</u>		
	<u>Black</u>	<u>White</u>	<u>Black</u>	<u>White</u>	<u>MUST</u>
Flammability					
Limiting Oxygen Index	33	44	38	47	31
Method 5903					
After flame, sec	0	0	2	0	0
After glow, sec	0	0	0	0	0
Char length, cm	10.7	9.4	10.6	6.3	6.6
Method 5905					
After flame, sec	5	0	4	1	6
Percentage consumed	100	64	44	34	60

In any discussion of gloves or coated fabrics, especially for military applications, the subject of permeability should be discussed. Conveniently, Firestone furnished values of  $Q$  (air permeability in cc) for silicone, polyphosphazene, neoprene, Hypalon, Kel F, Viton A, and butyl rubber. The values decreased in the same order listed 35.4, 8.5, 0.98, 0.96, 0.80, 0.79 and 0.46, all times  $10^{-7}$  cc tested at 176°F but corrected to "standard" conditions of 0°C and 760 mm Hg  $\text{sec}^{-1} \text{cm}^{-2} \text{atmos}^{-1}$ . From this listing we can see that polyphosphazene is more impermeable than silicone rubber, but is an order of magnitude more permeable than the other common elastomers.

## GASKETS

In addition to the glove, Fig. 2 showed a picture of a gasket. This gasket is somewhat typical of the two items that did get into the supply system. Items can be adopted by means of a requirements document or by the natural progression from research and development projects, to prototypes, to small production buys, and finally to a technical data package. The items to be discussed today arrived by a different route -- the unsatisfactory equipment report.

The first unsatisfactory equipment report from Alaska concerned the adaptor for the Yukon stove. When one tightened the adaptor at extremely cold temperatures, it broke. The fault lay with a nitrile gasket which got so stiff, it increased the torque required to turn the adaptor, which then cracked. A mold was made in-house, and several hundred gaskets were prepared from polyphosphazene by Mr. Mahoney of our laboratory. The turn-around time was short because we had the Firestone polyphosphazene material available. This is important, because the pressure for response to a quality deficiency problem within weeks is intense. The actual gasket is shown in Fig. 3.

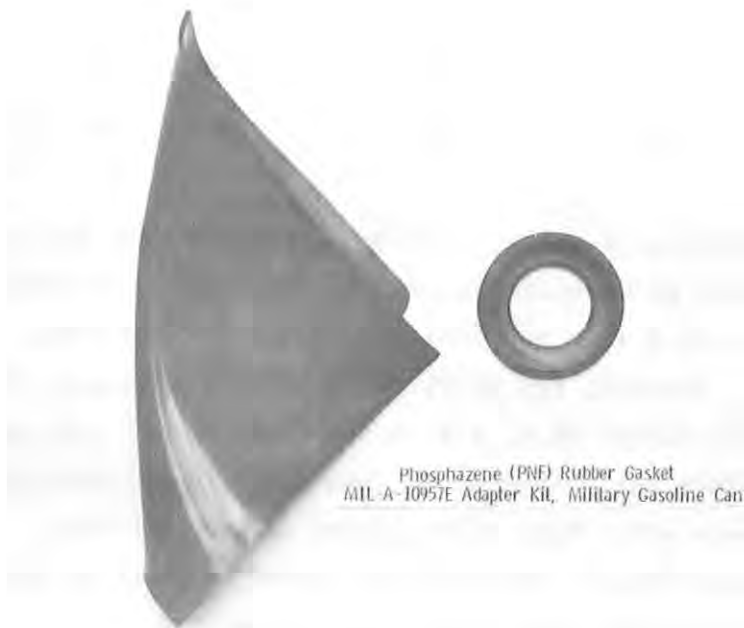


FIGURE 3. Polyphosphazene gasket for Adapter Kit.

In 1981, another unsatisfactory equipment report arrived from Alaska. The main gasket on the five-gallon can leaked at cold temperatures down to -50°C. Field fixes such as using two gaskets were not satisfactory, and we were given 30 days to correct the problem. This time personnel at Ft. Richardson still might not have known the chemistry or name of the polyphosphazenes, but they did know and then let us know that they wanted the same material we had used for the stove adaptor. It was Firestone compound PNF 270-003R cured with Vulcap for 20 minutes at 340°F followed by a 350°F four-hour post bake. The number of large gaskets made for the closure cap is not known but, by 1981, 1200 of the small gaskets for the adaptor kit had been produced.

#### Helicopter Seals

This project was carried out under a customer order from Material Technology Laboratory (formerly Army Materials and Mechanics Research Center), Watertown, MA, while the Natick work consisted of compounding studies.<sup>15</sup> The target properties were a Shore A durometer of 75-90, a tensile strength of 1500 psi, a minimum elongation of 175%, and maximum changes on aging at 150°C for 70 hours of a 25% drop in tensile strength, 30% drop in elongation, and an increase in hardness of 10 points. The properties were reached or exceeded but, perhaps more important, consider- and Vulcup 40 KE (40%  $\alpha,\alpha$ -bis (t-butylperoxy) diisopropylbenzene on silane-treated clay). As reinforcing fillers, fumed silicas and silane-treated clays were superior to carbon blacks.

## Flame Resistant Treatments.

The previous applications have centered around the use of the fluoroalkoxy polyphosphazenes because of their low temperature properties. The fluorinated substituents add considerably to the cost therefore the aryloxy polyphosphazenes are worth considering if one can accept the considerably higher glass transition point. Singler listed the glass transition points for various substituted polyphosphazenes with the simplest aryloxy polymer possessing a glass transition temperature of about 50°C but with some substituted aryloxy polymers being more flexible with glass transition temperatures of -25°C.<sup>4</sup> As Singler points out, the aryloxy groups which have meta substituents lead to polymers with lower glass transition temperatures while the parasubstituted aryl groups (methyl, chloro) are only as flexible as the parent aryloxy. Lengthening the size of an alkyl group in the para position again decreases the glass transition temperature, by 18°C. In any event, use of cheaper polyphosphazenes allows one to consider closed cell foams, open cell foams, and coatings -- all conferring flame resistance to the article. Quinn and Dieck at Armstrong Cork investigated cellular polymeric systems based on polyaryloxy phosphazenes.<sup>16</sup> Without any halogen present, limiting oxygen indices of 32 to 38 were obtained and the smoke evaluation as measured by the NBS smoke density chamber was very low.

More recently scientists at Monsanto Chemical Company have developed a method of producing amidophosphazenes in a pilot plant operation. The product hexamido cyclotriphosphazene can be used as a textile finish with trimethylolymelamine to confer flame resistance. Heitsch also of Monsanto discusses the use of the amidophosphazene on cotton and makes some important points about flame retardancy.<sup>17</sup>

The first is that, although about 3% phosphorous is usually necessary to render cellulose fire-retardant, when sufficient nitrogen is present (7%) the phosphorous content could be as low as 1%. The other important point made by using model compounds is that the atomic ratio of carbon to phosphorous should be as low as possible in a flame retardant to have a high limiting oxygen index. In other words, carbon in the fire retardant

is many times more deleterious than one would expect from its relative contribution to the fuel. For these reasons the amidophosphazenes, and in fact most phosphazenes, are natural candidates for flame retardancy not only in themselves but as additives.

The amidophosphazenes were effective on cotton as pointed out by Heitsch, and this is important for items such as children's sleepwear when they are all cotton. The military has a greater interest in conferring flame retardancy to blends such as nylon-cotton, and this use of polyphosphazene on blends has lagged their use on cotton.

#### FOAMS

In the case of foams there is a need not only for flame resistance but also for minimum smoke production. At USANRDEC the aryloxy phosphazenes were compounded in various ways and with various blowing agents. Among the latter were sodium bicarbonate, ammonium bicarbonate, Unicel (N,N - dinitroso pentamethylene tetramines), Celogen AZ (azodicarbonamide) and Celogen OT (P,P Oxy bis (benzene sulfonyl hydrazide). Moderate success was achieved in obtaining successful foams with densities in the region of  $0.3 \text{ g/cm}^2$ . One of the resulting foam samples was tested by Quinn and Dieck at Armstrong Cork Company.<sup>16</sup> The Rohm and Haas XP2 Smoke Value test was conducted because of its ease of use with small samples. The maximum smoke percentage obtained was 13% as contrasted with ordinary materials giving heavy smoke in the 75% range. Quinn and Dieck prepared foams on their own with varying amounts of the filler, alumina trihydrate (50 to 175 parts per hundred parts of polyphosphazene). Excellent flame retardant properties were obtained (LOI's of 32.2 to 38.7) with little smoke evolution measured by the NBS Smoke Density Chamber. Similar work was conducted at Horizons Research, Inc. by Thompson and Reynard that also resulted in products with good flame retardancy, little smoke and sufficient strength (50 psi) for most purposes. The Naval Ship System Command sponsored the latter work.

More recently (1986) Dr. Mueller of Ethyl Corporation reviewed the use of the aryloxy polyphosphazenes foams under the trade name Eypel-A.<sup>18</sup>

Foams were produced using a free expansion process in a hot air oven to decompose the chemical blowing agent generally to give nitrogen. The foam is closed cell with a skin approaching the density of the base polymer. Evaluators refer to the "Quarter Scale Modeling of Room Fires" by NBS<sup>19</sup> and to flammability-toxicity ratings by Lieu, Magell and Alarie for rating these foams.<sup>20</sup> In the quarter scale test no flashover was indicated as contrasted with PVC/Nitrile foam (flashover at the same heat input 640 Btu/min) and FR-polyurethane foam (flashover at 320 Btu/min). Analyses of combustion products confirms the relative safety of the polyphosphazene products compared to a product like polyvinyl chloride.

#### Other Applications

Other recent applications included that of the preparation of membranes for use in harsh environments. The trifluoroethoxy polyphosphazene has been used in experiments by the Department of Energy's Idaho National Engineering Laboratory in Idaho Falls to develop membranes. The membranes have been between 0.1 and 10 microns thick and prepared by dip casting and spin casting.<sup>21</sup> The ultimate in a useful material for military purposes would be the use of a polyphosphazene type material which would be applied to a fabric in low concentration. The fabric would remain permeable with perhaps increased water vapor transport properties to allow evaporation of perspiration. It would also confer water-, oil-, and flame-resistance at a low add-on.

#### Future of Polyphosphazenes

The greatest amount of new work published on synthesis, properties and applications of polyphosphazenes is by Singler at the U. S. Army Material Technology Laboratory in Watertown and by Professor Allcock at the University of Pennsylvania.<sup>22,23</sup>

Allcock's group at Pennsylvania State University is preparing various derivatives of polyphosphazenes which may lead to other polymerization monomers and thus to polymers with more varied applications.

Allcock's group has devoted a major effort recently to the synthesis of transition metal derivatives of phosphazenes with potential applications as immobilized catalysts, high temperature polymers or electroactive materials. Previously he developed an improved method for obtaining the phosphazene polymers based upon the use of a solid/liquid phase transfer agent, tetra-n-butylammonium chloride, in the phosphazene-sodium alkoxide reaction. The result was a faster reaction at a lower temperature.

Other work on synthesis conducted at Texas Christian University takes a very different direction. Dr. Neilson has synthesized polyphosphazenes in which the aryl and alkyl groups are directly attached to the phosphorous atom into the backbone allowing many interesting precursors to be prepared. The lack of emphasis on fluoroalkoxy substituents may lead to lower cost materials and wider usage. The direct attachment of the alkyl and aryl groups to phosphorous leads to higher thermal stability but raises the glass transition point somewhat. Dimethyl substituents give a Tg of  $-45^{\circ}\text{C}$  as contrasted with  $-60^{\circ}\text{C}$  for the dimethoxy substituents.<sup>24</sup>

Allen at the University of Vermont has focused his attention on olefinic phosphazenes.<sup>25</sup> The aim is to allow the phosphazene to be introduced into a host of materials by copolymerization or reaction. As a minimum it would be a way of conferring flame resistance to a resultant copolymer. The homopolymerization of the phosphazenes containing an acetylenic function interests Allen because of electronic applications related to photo- and semiconducting behavior.

Allen has also shown that certain phosphazenes surgically implanted can be used in cancer chemotherapy. These phosphazenes have alkylating groups as substituents.<sup>26</sup>

## CONCLUSIONS

The work conducted at Natick RD&E Center on polyphosphazenes has shown the following:

(1) Less than an ounce of an elastomer can be compounded and enough practical values of low temperature flexibility, tensile strength, oil resistance, and heat stability obtained to generate enthusiasm for further support and work.

(2) To date two items prepared from polyphosphazene have been introduced into the system. The applications (gaskets) have been critical and small in size.

(3) There are applications such as gloves, coated fabrics, and fabric treatments waiting to be developed. This will require more research and could markedly increase the volume utilized. The gloves need not be monolithic; a phosphazene coating over butyl may be indicated.

(4) Compounding studies have been highlighted in this discussion, but the future policy of manufacturers such as Ethyl Corporation will be to control compounding and to supply proprietary materials without disclosing the details. Hopefully, this disclosure of our in-house compounding studies and of the limitations of our prototype materials will help them to help us.

This document reports research undertaken at the US Army Natick Research, Development and Engineering Center and has been assigned No. NATICK/TR-87/035 in the series of reports approved for publication.

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### List of Low Temperature Methods

#### D-746-79 "Brittleness Temperature of Plastics and Elastomers By Impact"

One inch long specimens, one-fourth of an inch wide and 75 mil thick are impacted at 6-7 ft/second. Temperature of failure (separation or visible crack) is the brittleness temperature.

#### D-797-82 Rubber Property "Young's Modulus at Normal and Subnormal Temperatures"

This is a flexure test conducted at different temperatures until some limiting value is obtained

#### D-1043-84 "Stiffness Properties of Plastics as a Function of Temperature By Means of a Torsion Test"

This test is sometimes called the Clash-Berg Torsional Tester.

#### ASTM-D-1053-79 "Measuring Rubber Property Stiffening at Low Temperature Using a Torsional Wire Apparatus"

Samples are twisted 180° and the angular twist reading on the dial is taken 10 seconds later. The lower the reading the stiffer the material. A complete plot of twist angle vs temperature is obtained from which temperatures are identified corresponding to various multiples of the original torsional modulus.



A P P E N D I X

# APPENDIX

TABLE A-1. List of Terms Used in Text

<u>Term</u>	<u>Explanation</u>	<u>Use</u>
<u>Aerosil 200</u>	Colloidal Silica	reinforcement
<u>Altax (MBTS)</u>	Benzothiazyl disulfide -	accelerator
<u>Butyl Zimate</u>	75% Tetrone A in EPR Binder	accelerator
<u>Cadox</u>	2,4 - Dichlorobenzoyl Peroxide in Silicone Fluid	curing Agent
<u>Captax (MBT)</u>	2 - Mercaptobenzothiazole	accelerator
	Diethylene Glycol	accelerator
<u>Dicup 40 C</u>	40% Dicumyl Peroxide supported on Calcium Carbonate	
<u>FEF Black N550</u>	Like Sterling SO-N550	medium reinforcement
<u>HAF Black N330</u>	High abrasion Black	good reinforcement
<u>Hydral 710</u>	Hydrated aluminum oxide	
<u>Methyl Tuads</u>	Tetramethylthiuram Disulfide	accelerator
<u>Firestone K-17217</u>	51.3% (OCH <sub>2</sub> CF <sub>3</sub> ); 49.7% OCH <sub>2</sub> (CF <sub>2</sub> ) <sub>3</sub> CF <sub>2</sub> H; 5% cure sites	phosphazene gum
<u>Firestone K-17638</u>	49.9% (OCH <sub>2</sub> CF <sub>3</sub> ); 49.7% OCH <sub>2</sub> (CF <sub>2</sub> ) <sub>3</sub> CF <sub>2</sub> H	phosphazene gum
<u>Firestone K-17640</u>	64.1% (OCH <sub>2</sub> CF <sub>3</sub> ); 26.6% OCH(CF <sub>2</sub> ) <sub>3</sub> CF <sub>2</sub> H; 8.7% or 1.48% cure sites	phosphazene gum
<u>Methyl Zimate</u>	Zinc Dimethyl Dithiocarbamate	accelerator
<u>DTDM</u>	4,4l - dithiodimorpholene	accelerator

<u>Term</u>	<u>Explanation</u>	<u>Use</u>
<u>Santocure (CBTS)</u>	N-Cyclohexyl-2-Benzothiozole Sulfeneamide (Monsanto)	
<u>Silanox 101</u>	Hydrophobic Fumed Silica	reinforcing filler
<u>Sterling SO N550</u>	Fine extrusion furnace carbon black - large particle size, high structure	
<u>Sulfasan</u>	76% DTDM	accelerator
<u>Tellurac</u>	Diethyl Dithio - Carbamate Vulcup - BIS (t-Butyl Peroxy) Diisopropylbenzene	accelerator curing agent
<u>XLC Magnesia</u>	Magnesium Oxide	
<u>Vanax</u>	See DTDM	

TABLE A-2. Compounding Studies Utilizing  
the Polymer 1408-12 (Horizons Inc)

COMPOUND INGREDIENTS	COMPOUND NUMBER				
	<u>1C</u>	<u>1C (A)</u>	<u>5C</u>	<u>6C</u>	<u>7C</u>
POLYMER	100	100	100	100	100
DICUP 40C <sup>a</sup>	4	4	4	- -	- -
CADOX TS50 <sup>b</sup>	- -	- -	- -	1.5	1.5
MGO	5	5	5	- -	5
HYSIL 233 <sup>c</sup>	15	15	15	15	15
HEAT TREATING	- -	1 hr/300°F	- -	- -	- -
BIN AGING	- -	- -	2 wks	- -	- -
OVEN CURE					
MINS/°F	60/290	60/290	60/290	15/240	15/240
TENSILE, psi	433	469	594	Weak & cheesy	285
ELONGATION	230	230	200		270

<sup>a</sup> 40% Dicumyl Peroxide Supported on Calcium Carbonate

<sup>b</sup> 50% 2,4 Dichlorobenzoyl Peroxide in Silicone Fluid

<sup>c</sup> Precipitated Hydrated Silica Reinforcing Fillers

TABLE A-3. Properties of the Elastomers  
of Military Interest

	VOLUME SWELL <sup>a</sup> %	LOW TEMP T <sub>5</sub> <sup>b</sup> (°F)	HEAT RESISTANCE °F	FLAMMABILITY BURN SUPPORT in Flame Combustion	WEATHER AND OZONE RESISTANCE	HYDROSTATIC STABILITY
PHOSPHAZENE	7	-55	350 <sup>c</sup>	No No	Good	Good
FLUOROCARBON	0	+15	425	Yes No	Excellent	Excellent
NATURAL	200	-60	250	Yes Yes	Poor	Good
SBR	150	-35 to -50	250	Yes Yes	Poor	Good
EPDM	100	-50	275	Yes Yes	Excellent	Good
NEOPRENE	80	-20	250	Yes No	Good	Poor to Fair
NITRILE	25 to 60	+15 to -20	275	Yes Yes	Poor	Excellent
POLYSULFIDE	10	-40	250	Yes Yes	Good	Excellent
SILICONE	200	-40 to -70	450	Yes Yes	Excellent	Excellent
FLUOROSILICONE	20	-70	400	Yes No	Excellent	Excellent
EPICHLOROHYDRIN	20	-30	275	Yes Yes	Excellent	Fair to Good

<sup>a</sup> In 70/30 Isooctane/Toluene

<sup>b</sup> Torsional Stiffness: Temperature at which material is approximately five times stiffer than at room temperature

<sup>c</sup> Based on weight loss results

TABLE A-4. Thermoplastic Elastomers

<u>Olefinics</u>	<u>Company</u>
Polytrope	A. Schulman
Telcar	Teknor Apex
Santoprene	Monsanto
#2277	Prolastomer
Alkrin	Du Pont
 <u>Block Polymers (SBS)</u>	
Kraton	Shell Chemical Co.
Solprene	Phillips Petroleum
 <u>Polyester</u>	
Hytrel	Du Pont
Gaflex	GAF Corp.
 <u>Polyurethanes (Pellets)</u>	
Estane	B.F. Goodrich Co.
Texin	Mobay Chemical Co.
Pellethane	CPR Div., Upjohn Co.
 <u>Polyurethanes (Castables)</u>	
Castethane	Upjohn Co.
Conathane	Conap Co.
Cyanaprene	American Cyanamid
Multrathene	Mobay Chemical Co.
Solithane	Thiokol Chemical Co.
Palothane XPE	Polaroid
 <u>Olefinic Copolymers</u>	
Elvax (EVA)	Du Pont
Neodol (Ethylene-Propylene)	Du Pont